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(54) Title: METHOD OF PRODUCING PROTEIN SHEATHS AROUND FIBERS OF TEXTILES AND TEXTILES PRODUCED THEREBY

(57) Abstract: The present invention is directed to a method for treating a synthetic, man-made or natural fiber substrate to create a permanently attached protein sheath around each fiber of the substrate. Such a treatment gives a composite substrate that exhibits the most desirable characteristics of the fiber core coupled with the most desirable characteristics of the protein sheath. It is also possible to apply this technology to individual synthetic fibers or yarns, if desired, before weaving, knitting, stitch-bonding or other method of woven or non-woven substrate formation.

METHOD OF PRODUCING PROTEIN SHEATHS AROUND FIBERS OF TEXTILES AND TEXTILES PRODUCED THEREBY

BACKGROUND OF THE INVENTION

The use of synthetic fabrics and blends by consumers has decreased over recent years in favor of 100% woolen fabrics which offer preferred appearance and comfort; especially in apparel. However, the use of woolen yarn and fabrics also has its disadvantages. Primarily, fabrics made entirely of natural wool tend to shrink and felt upon washing, hence they must be dry cleaned instead of laundered, which is expensive and requires the use of carcinogenic solvents. Also, the wrinkle resistance of these fabrics is not as good as synthetics. The most popular method of controlling wool shrinkage, felting, and wrinkling for apparel outerwear is to react the wool fabric with resins made of formaldehyde and coat the fibers with a "lubricating" polymer to decrease the amount of felting. However, formaldehyde is considered to be a hazardous chemical and dangerous to handle during processing. It is also considered dangerous on the fabrics that come into contact with the body because formaldehyde is a known carcinogen. Additionally, formaldehyde-based resins, when used to control the shrinkage and felting of wool or wool blend fabrics, degrade the abrasion resistance and strength properties of the fabric and make them more prone to fabric holes and scuffing. Although non-formaldehyde resins have been invented (e.g., polycarboxylic acids), they are less effective, more expensive, and equally prone to fabric strength loss. The addition of "lubricating" polymers also changes the hand of the fabric, giving it a more synthetic feel. Due to these problems, very few commercially-made wool fabrics are treated to control shrinkage, felting and wrinkling.

With the advent of synthetic textile fibers (such as, for example, polyester, polyamide, polyacrylamide, polyolefin, polyacrylate, and nylon), the possibility arose for producing continuous filament yarns with greater strength and more durability than those formed of staple fibers, and also with fewer wrinkling and shrinkage problems. The shrinkage of these fabrics can be controlled by using a yarn where the heat annealing point of the synthetic fiber polymer has been exceeded. Products made from synthetic yarn have excellent strength properties, dimensional stability and good color fastness to washing, drycleaning, and light exposure. The use of 100% polyester knit and woven fabrics became extremely popular during the late 1960s and through the 1970s. More recently, continuous filament polyester fiber has also been cut into staple that can then be spun into 100% staple yarns or blended with wool or other natural fibers. However, synthetic yarns and fabric made from these yarns have many undesirable properties, including a shiny, synthetic appearance, a slick, artificial tactile "feel", limited moisture transport ability, and a tendency to accumulate

static charge. Additionally, polyester fiber is prone to pilling in staple form and picking in continuous filament form.

Several attempts have been made to produce fabrics with the positive qualities of both wool and polyester fibers without their negative attributes. Such attempts have included blending and sheath/core yarn spinning. These methods require modifications on the fibers/yarn and were not possible on fabric until the current invention.

Conventional methods of blending wool and synthetics together have been less than fully successful as both mechanical and intimate blends of polyester and wool tend to pill, pick, shrink, and can be uncomfortable to wear. The consumers' use of polyester and polyester-blended fabrics has been reduced over recent years in favor of 100% wool fabrics, which offer preferred appearance and comfort.

US Patent 5,622,531 discloses a method of applying water-soluble wool protein to polyurethane fabric using chitosan as an adhesive layer for the purpose of increasing the hydrophilicity of the polyurethane fabric. This process is specific to polyurethane and no attempt is made to form a covalent bond between the textile, chitosan, or the wool protein layers – i.e., only weak non-covalent forces are employed to hold the protein layer to the polyurethane.

Accordingly, there is a need in the art to produce fabrics that have both the positive qualities of wool and synthetics while eliminating their respective negative qualities, the process also being fast, economical, durable, applicable to many types of fabrics, and transparent to current textile manufacturing practices, such as sanding, weaving, and dyeing.

SUMMARY OF THE INVENTION

The present invention is directed to a method for treating a fabric, garment, woven good, or non-woven good (encompassed herein under the term "substrate" or "fibrous substrate") made from synthetic fibers to create a permanently attached protein sheath around each synthetic fiber of the substrate. Proteins have the desired properties of wool, which is formed from proteins. Such a treatment gives a composite substrate that exhibits the most desirable characteristics of the synthetic core, coupled with the most desirable surface characteristics of the natural, protein sheath. For example, it will exhibit the mechanical properties of the synthetic core fiber and wool-like surface properties. It is also possible to apply this technology to individual synthetic fibers or yarns, if desired, before weaving.

More particularly, in the process of this invention, an article or fibrous substrate that contains synthetic hydrophobic fibers is contacted with an aqueous solution that contains

water-soluble (oxidized) protein polymers or monomers. The protein monomers/polymers are then reduced and/or crosslinked to each other and to the fiber using a suitable crosslinker to form a durable protein sheath or encapsulation layer around the hydrophobic fiber. The resulting composite synthetic substrate exhibits the desirable properties of proteins (such as non-shiny appearance, wool-like hand, water absorption and breathability, comfortable feel next to the skin, and the like) while retaining desirable properties of the synthetic material (such as strength, good color fastness, and lack of wrinkling or shrinkage), even after repeated launderings. One advantage of this method is the ability to apply it by performing a pad/dry/cure process directly to dyed and finished synthetic fabrics, which is economical and easily accomplished with currently used textile equipment.

The present invention is further directed to a method of treating a fabric, garment, woven good, or non-woven good ("substrate" or "fibrous substrate") made of natural fibers, or individual natural fibers or yarns to create a permanently attached protein sheath or encapsulation layer around the fibers of the substrate. This imparts the desirable properties of a cotton-like surface while retaining some of the functional properties of the core natural fiber.

According to the present invention, it is possible to incorporate other components into the encapsulation layer to impart durable attributes to the synthetic or natural fiber or fabric. In this way, the protein layer acts as a binder to encase not only the substrate fiber but also the compound to be incorporated into the outer layer.

DETAILED DESCRIPTION OF THE INVENTION

As used herein and in the appended claims, "a" and "an" mean "one or more".

In the preferred embodiment of the invention, the synthetic, man-made or natural core material in fabric or other fibrous substrate form is passed through a bath containing an aqueous solution of water-soluble (oxidized) protein and crosslinker and, if necessary, a suitable crosslinker catalyst. This bath is referred to herein as the "protein polymer sheath formulation" or "sheathing formulation". The fabric or substrate is padded to remove excess liquor, heated to dryness, then cured at a temperature sufficient to cause reaction between the crosslinker, the core material, and the protein. Crosslinks are formed between these compounds to form a thin film of protein on the surface of the core. This layer is referred to herein as a "protein encapsulation layer", "protein sheath", "sheathing layer" or "sheath". . The same general method can also be applied to individual fibers, ribbons, and shaped materials. Application can also be achieved by spraying, foam, or any other means known in the art for contacting a substrate with a treating solution. Alternatively, the fabric first can be dipped in the bath with the solubilized protein and crosslinker, then optionally sprayed with or

dipped into a second bath containing an acidic reducing agent that regenerates the original insoluble protein structure.

Non-limiting examples of water-soluble protein polymers include chemically oxidized wool, gelatin, sericin, albumin, collagen, etc.

The water-soluble protein polymers are prepared by the oxidative destruction of a protein, such as wool, for example, which is carried out in a weakly alkaline liquid medium containing an oxidizing agent. The liquid medium is preferably an aqueous medium, although alcohols such as methanol, ethanol, or the like, may be used, either alone or in combination with water. The liquid medium is made weakly alkaline by the addition of a pH adjuster, which may be selected from, but is not limited to, ammonia, alkaline metal hydroxides, amines, alkaline metal carbonates, and the like. These may be appropriately selected according to the kind of liquid medium and oxidizing agents to be used.

Examples of oxidizing agents are well-known in the art and include, but are not limited to, peroxides such as hydrogen peroxide, peracetic acid, performic acid, and the like. Hydrogen peroxide is presently preferred because it is inexpensive, easily handled, and easily treated to destroy excess harmful waste .

The solubilization rate of the protein varies depending on the protein, the type and concentration of the oxidizing agent, and the kind of dissolving medium used. The solubilizing time is normally about 0.1 to about 1.0 hour. The resulting solubilized protein contains the functional groups of its constituent amino acids, such as hydroxyl, amine, and carboxylate groups, which may be used with a crosslinking agent such that the protein is adhered to itself by covalent bonds to durably attach a sheath of the protein to a synthetic, man-made or natural fiber.

Any compound capable to bonding to two or more nucleophiles (e.g., hydroxyl, amine, thiol, etc) can be used as a crosslinker to link the hydroxyl, thiol, amine, and carboxylate groups on the solubilized protein, preferably wool protein, sheath to the synthetic or man-made core. Currently preferred crosslinkers are epoxides. Epoxide crosslinkers include epichlorohydrin, polyethylene glycol-diepoxide terminated, or any other monomer or polymer containing two or more epoxide groups. These species react with nucleophilic groups, preferably amines and thiols. One skilled in the art would recognize that there are more crosslinking chemistries than presented here. For example, blocked isocyanates and crosslinkable siloxane polymers could be employed. Polycarboxylic acids and methylol compounds can be used in a two-dip process. That is, methylol compounds and polycarboxylic acids cannot be used in the same solution as the alkaline oxidized wool because they require acidic conditions to crosslink and acid causes the oxidized wool to precipitate. However, the soluble wool can be first padded onto the substrate, after which

the acidic methylol compound or polycarboxylic acid can be padded on – i.e., a two-step process. Epoxid s, on the other hand, crosslink under basic conditions; thus, the soluble wool and epoxide crosslinker can be placed together in the same bath.

While there are many crosslinking chemistries that would allow one to form a proteinaceous polymeric sheath about a fiber, the following are presently preferred methods: epoxides in a one dip procedure; anhydride chemistries (e.g., polycarboxylic acids) with or without sodium hypophosphite catalyst in a two-dip process; and N-methylol compounds (e.g., DMDHEU) with magnesium chloride catalyst in a two-dip procedure.

The temperature of the treatment solution of oxidized protein and crosslinker should not be so high as to decompose the reactants or so low as to cause inhibition of the reaction or freezing of the solvent. The time required for the crosslinking processes herein will depend to a large extent on the temperature being used and the relative reactivities of the starting materials. Therefore, the time of exposure of the textile to the oxidized polymer in solution can vary greatly, for example from about one second to about two hours. Normally, the exposure time will be from about five to about ten seconds. Following exposure, the treated yarn or fabric is dried at ambient temperature or at a temperature above ambient, up to about 100°C. After drying, the fabric is cured if polymerization does not take place during the drying step. Unless specified to the contrary, the processes described herein take place at atmospheric pressure over a temperature range from about 80°C to about 180°C, more preferably from about 110°C to about 160°C, and most preferably at about 150°C. Unless otherwise specified, the process times and conditions are intended to be approximate.

The present invention is further directed to the hydrophobic yarns, fibers, fabrics, finished goods, or other textiles (encompassed herein under the terms "textiles", "substrates" and "fibrous substrates") treated with the proteinaceous fabric finishes of the invention. These textiles or substrates will display improved wettability and moisture permeability compared to traditional synthetic and some man-made textiles. In addition, other properties of the fiber may be modified by treatment, such as fiber shininess, fabric feel or "hand", static dissipation ability, and fiber-fiber abrasion noise characteristics.

Properties imparted by the protein sheath or encapsulation layer do not disturb the macro properties of the fabric; that is, the sheath does not significantly increase the diameter of the fibers, it does not fill spaces between fibers or clog the fabric with large pieces of protein, and the like. Additionally, the treated fabric feels like wool to the touch, rather than like polyester, and exhibits improved wettability.

The synthetic and man-made textiles prepared according to the present invention can be used in a variety of ways including, but not limited to: clothing, upholstery and other home furnishings, hospital and other medical uses, automobile applications, and the like;

and industrial uses, such as those listed in Adanur, S., *Wellington Sears Handbook of Industrial Textiles,* p. 8-11 (Technomic Publishing Co., Lancaster, PA, 1995).

Some properties can be imparted to textile articles by processing in garment form, including a soft hand, shrinkage control, durable press, and unusual and unique appearances, depending on the process used. Lava stones, pumice, bleach, and/or protein kinase enzymes may be used to accelerate abrasion and impart a worn look to the garment. These and similar post-treatment processes can be applied to the current invention to improve the aesthetic appeal of the final garment. The protein sheath encapsulating the synthetic, man-made, or natural fibers allows post-treatment processing techniques to be applied to the treated synthetic, man-made, or natural fabrics of the present invention.

Incorporation of Auxiliary Components Within the Sheathing Layer

The application of a protein encapsulation layer to a fabric according to the present invention offers the opportunity to simultaneously finish the fabric with auxiliary components that do not have the innate ability to bind durably to the fabric. In this way, the protein sheathing acts as a binder to impart durability to non-substantive auxiliary components that are co-applied with the sheathing finish. Alternatively, the auxiliary component may have substantivity to the protein finish and can be applied in processing after application of the protein encapsulation layer. In either method, the base fabric is endowed with a number of properties that cannot be attained without the use of the encapsulation layer.

Some examples of auxiliary components include infrared-absorbing compounds that can be permanently incorporated onto the fabric to minimize detection from night vision equipment. Examples of infrared-absorbing material are carbon black, chitin resin, or in general, compounds that absorb electromagnetic radiation of wavelengths from 1000 to 1200 nm. Fabric treated with an encapsulating layer containing infrared-absorbing materials accrue infrared absorptive ability as well as other beneficial properties belonging to the encapsulating layer; such fabric may be of particular interest in military applications.

Similarly, ultraviolet light-blocking compounds can be incorporated to protect either the wearer of the garment or the fabric material itself from ultraviolet rays. Colored pigments or dyes may be incorporated in the outer layer to dye the fabric. Magnetic colloids can be embedded in the sheath to provide data storage capabilities to the fabric. Bio-active agents (such as insect repellants, anti-microbials, and pharmaceuticals, for example) may also be incorporated, as well as flame-retardant chemicals and anti-static agents. Odor-absorbing compounds and neutralizers (e.g. activated charcoal or cyclodextrins) or, alternatively, a material that one wishes to release in a prolonged fashion by using, for example, hydrolyzable linkers, may also be applied according to this invention.

In one embodiment, colloids, generically described as particles with a mean diameter between 10 and 500 nanometers, are incorporated into the encapsulating sheath formulation and bound to the treated fabric. Colloid particles are too small to be seen even with conventional microscopy, so the individual particles will not be noticeable on the fabric. However, certain metal colloids such as gold and silver are of particular interest due to their light-absorptive properties. Metal colloids absorb light at a maximum absorption wavelength related to metal type and particle size. They have found extensive use in inventions relating to biological and toxicological assays.

US Pat. 5,851,777 issued to Hunter et. al. discloses the use of colloidal particles bound to ligands that specifically bind a certain biological or toxicological moiety. Colored metal colloids are specifically claimed as one aspect of the invention. When the specific biological or toxicological moiety is added to a solution containing the ligand-bound metal colloidal particles, ligation to the moiety results in particle aggregation and a shift in the maximum absorption wavelength (i.e. solution color). Hunter et al. also disclose a number of related patents utilizing ligand-bound colloid particles. An important aspect of these inventions is the capacity to bind the ligand to the particle surface via an intermediary polymer. The intermediary polymer is either physically entrained (in part) within the particle or is durably adsorbed to the particle surface. The intermediary polymer of necessity contains reactive groups enabling it to bind to the ligand. The disclosures of USP 5,851,777 and those cited therein are incorporated herein by reference.

US Pat. 6,136,044 issued to Todd discloses the use of metal colloids to color substrates such as fibers, yarns and textiles. The substrate to be colored is first placed in a bath containing a reducing agent, preferably an agent that has some substantivity to the substrate. After allowing sufficient time for the reducing agent to adsorb, the substrate is removed from the bath, optionally dried, then placed in a second bath containing a dissolved metal salt corresponding to the metal colloid of interest. The adsorbed reducing agent reduces the salt to the colloid and serves as a nucleating site for particle growth. The resulting particle is adsorbed to the substrate or optionally entangled with the substrate. The substrate is thereby colored with a shade that corresponds to the parameters of metal type, particle size, and amount of metal on the substrate. As each of these parameters can be controlled, a variety of shades can be accessed. The resulting color of the substrate is both wash-fast and light-fast. This method does not require the use of a polymeric binder or other agent to provide colorfastness.

Certain metal colloidal suspensions, specifically silver and copper and more particularly silver, have demonstrated biocidal activity against a broad spectrum of bacterial

species. The Merck Index (10th edition) maintains that silver "has been used for purification of drinking water because of toxicity to bacteria and lower forms of life".

In on embodiment of this aspect of the invention, metal colloids are incorporated into the sheathing formulation to provide coloring to substrates treated with the formulation. In another embodiment of this aspect of the invention, metal colloids with antimicrobial activity, preferably silver and copper, most preferably silver, are incorporated into the sheathing formulation. Substrates treated with this formulation are endowed with antimicrobial activity. In another embodiment of this aspect of the invention, metal colloids are incorporated into the sheathing formulation in sufficient amount to facilitate electrical conductivity on the surface of a treated substrate, whereas the untreated substrate has little or no electrical conductivity properties. The treated substrate thereby receives anti-static properties.

The metal colloids may be incorporated into the sheathing formulation by a variety of methods. In one method, the metal colloids are prepared and then added to the sheathing formulation. The metal colloids may be prepared by reduction of metal salts via chemical, electrochemical or irradiative processes which are known to those of skill in the art. For example, silver salts may be reduced to metallic silver with sodium borohydride (chemical), an electric potential (electrochemical) or with visible light (irradiative). So-called "passivating agents" may be employed in the formation of the metal colloids; these agents may serve as nucleating agents for particle growth and also coat the particle surface to minimize particle aggregation. Common passivating agents include bovine serum albumin, casein, and bovine milk proteins (e.g. powdered milk). Preferably, the passivating agents contain functional groups that react with the components of the sheathing formulations. More preferably, the passivating agents are physically entrained within the colloidal particle to facilitate entrapment of the colloidal particle within the sheath layer.

The metal colloids may also be prepared directly within the sheathing formulation solution or with one or more of the components. A soluble metal salt of the colloid of interest is mixed with between one and all components of the sheathing formulation and then exposed to reductive conditions that induce colloid formation. This approach offers a potential advantage in that a viscous solution of between one and all components of the sheathing formulation can prevent aggregation of the nascent colloidal particles. Furthermore, one or more of the components of the sheathing formulation may function as a passivating agent for the colloid particles.

Incorporation of Colorants

In another embodiment, colorants can be anchored to the fiber using the current invention as a binder. The term "colorant", as used herein and the appended claims, refers

to either a pigment (water-insoluble) or a dye (water-soluble).

While one of the main aims of a protein encapsulating finish is to give a "natural fiber" (e.g., wool) feel to a synthetic fiber, the treated fiber has quite different chemical and physical properties from a wool fiber. There are at least three important differences:

First, the material that composes the finish may be only chemically similar, not identical to, a wool fiber. The chemical differences may have an important effect on the efficacy of various dye classes.

Second, the sheathing layer is highly cross-linked and thus tightly wrapped around the parent fibers. The sheathing layer cannot have significant ability to swell in water; if it did it would not be durable to laundering. Conventional dyeing relies extensively on swelling of the fiber to allow dye adsorption within the fiber; this maximizes both fastness and shade depth. Dyeing a sheath-wrapped fabric with conventional techniques that rely on fiber swelling may be ineffective.

Third, the sheath layer is very thin compared to the thickness of the fiber. Optimal even dyeing throughout the sheath without concomitant dyeing of the core fiber produces only a ring-dyed effect for the entire fiber. Many core fibers have substantivity for only a limited class of dyes, so the ring-dyed effect may be commonly observed when the sheath layer is dyed with a dye without substantivity to the core fiber.

The colorant may be chosen to match the color of the core fiber to give a deeper shade or, alternatively, the colorant could be chosen as a different shade to give a "two-toned" effect. Most likely, although not necessarily, a colorant would be chosen as a dark shade to be placed on top of a lighter-colored core fiber. The effect would be to have a "ring" dyed fabric. This type of dyeing is not easily performed on synthetic fabric, but is facilitated by the invention described herein. In one embodiment of the invention, the pigment would be dispersed in and co-applied with the encapsulating sheath. Another embodiment of the "two-tone" invention would be to have a separate dyeing step in the processing of the textile. The core fiber (dyed or undyed) would be treated with the protein outer layer and the fabric subsequently dyed with dyes that are substantive to the sheath. The dyes would be chosen to react or adhere to the outer surface and not the inner core, or vice versa. For example, a polyester fabric treated with the protein sheath could be selectively dyed with polyester-specific dyes for the inner core color (or none for white) and dyes specific for proteins to dye the outer layer. Some common dyes for the outer layer include dyes that will either: a) physically absorb (acid dyes), b) be mechanically retained (vat dyes and sulfur dyes), or c) be chemically reacted (reactive dyes) to the protein surface. This technique provides a way to make numerous effects and colors. Frosted (lighter color on top of darker), two-tone (two different colors), and "distressed" (outer layer can be

selectively abraded or hydrolyzed to get a worn look) effects are all possible via the present invention.

Methods of Col ring:

As used herein, the terms "one-step method" and "multiple-step method" refer to the number of steps required to process the fabric or substrate that is to receive a colored sheathing layer. The "one-step" method may require several steps prior to involvement of the substrate, but the colorant and sheath are applied to the fabric simultaneously. In a multi-step method, the colorant and sheath are applied in separate steps.

One-Step method: The most facile process is incorporation of the colorant into the base protein sheathing formulation prior to application of the finish to fabric. The colored formulation is then applied according to conventional methods such as immersion, spray, or padding, wherein the latter method is preferred. The colorant may be held within the sheath by such means as physical entanglement or encapsulation, electrostatic coordination, or chemical bonding to the sheathing material. Aside from simplicity of processing, another advantage this method provides is in attainable depths of shade. The sheathing layer is at most ten-fold less thick than the fabric fiber it encapsulates and is probably even smaller. Distributing the colorant evenly throughout the sheathing layer maximizes the amount of colorant applied. Even distribution also helps ensure that the colorant is "colorfast" or not easily removed by washing or other abrasive conditions. Potential disadvantages may include lack of equipment and/or reluctance within textile mills to apply colorant during finishing process, difficulty in achieving even application and depth of shade in padding process as well as cleanup and disposal problems for a colored sheathing finish.

Multiple-Step method: In this method, the colorant is applied to fabric that has previously been finished with a base protein sheathing formulation. The applied formulation may optionally include a component that has a particular affinity for the colorant. Alternatively, the finished fabric may be treated with a component with affinity to both the sheathing layer and the colorant prior to exposure to the colorant. A potential advantage of this method is the use of colorants that cannot be mixed into the sheathing formulation without altering the stability or durability of the sheath. Another advantage may be access to distinct aesthetic effects in comparison to the one-step method. Disadvantages include limitations on the types of effective colorants as well as probable surface accumulation of colorant with corollary problems of poor shade depth, crockfastness, and colorfastness. The sheathing layer is tightly cross-linked, which prevents the colorant from penetrating the layer to any significant depth.

Some specific descriptions of approaches to coloration with known dye classes are hereafter described. One or both of the methods described above may be applicable in these approaches.

Mordant Fixation: Certain metal species, called mordants, form strong bonds to chemical reactive groups such as carboxylate and phenol functionalities; the resulting mordant complexes do not dissociate in water and are often water-insoluble. As the mordant-reactive chemical groups are found on many types of dyes, mordant complexation provides a means of affixing an insoluble dye on or within a substance, particularly when the substance also complexes with the mordant metal. Mordant metals include chromium, cobalt, nickel, aluminum and zirconium.

In a one-step embodiment, the mordant and mordant-reactive dye are mixed into a base protein sheathing formulation. The mordant and mordant reactive dye are mixed into the formulation in an amount, order and manner that facilitate desired properties of the resulting colored formulation. Preferably, the resulting formulation is stable, e.g. the mordant complexes do not precipitate out. Stability is facilitated by mordant coordination to reactive groups on the water-soluble polymers of the base sheathing formulation. However, if the base sheathing formulation is sufficiently viscous, the mordant complexes may be adequately suspended within the formulation and water solubility may not be required. The mordant should be added in any amount desired up to the level where aggregation within the base sheathing formulation produces instability. The dye is added as desired up to an amount which fully utilizes the binding capacity of the added amount of mordant. The colored sheathing formulation is then applied to the substrate and the treated substrate is cured to affix the sheathing layer in place. The dye is bound durably within the sheathing layer by mordant complexation as well as by physical encapsulation.

In a multi-step embodiment, the mordant is mixed into a base protein sheathing formulation in an amount and manner that facilitate desired properties of the resulting mordant-modified formulation. Preferably, the mordant forms bonds to the sheathing material, but in any case the resulting formulation is stable, e.g. the mordant complexes do not precipitate out. Stability is facilitated by mordant coordination to reactive groups on the water-soluble polymers of the base sheathing formulation. However, if the base sheathing formulation is sufficiently viscous, the mordant complexes may be adequately suspended within the formulation and water solubility may not be required. The mordant should be added in any amount desired up to the level where aggregation within the base sheathing formulation produces instability. The mordant-modified formulation is then applied to the substrate and the treated substrate is cured to affix the sheathing layer in place. The sheath-wrapped substrate is then exposed to a mordant-reactive dye by techniques known

to those of skill in the art. In a preferred method, the substrate is exposed to a solution containing the dye at temperatures and for time periods that facilitate the reactive group(s) on the dye to complex with the mordant metals bound into the sheath. The dyed substrate is then dried. The dye is durably bound to the sheath layer by mordant complexation, but it is believed that the dye will only bind on the outer layer of the sheath layer due to the tight cross-linking within the sheath.

In another multi-step embodiment, sheath-wrapped substrate is exposed to mordant-metal solution. The mordant metal is exhausted onto the substrate by complexation with exposed reactive groups of the sheath material. The mordant-treated substrate is then removed from the solution, optionally dried, and then exposed to a solution containing a mordant-reactive dye. The dye is exhausted onto the sheath layer via complexation with the mordant on the sheath surface.

Other embodiments of this dyeing method are easily recognizable; although not described, all such are considered to be within the scope of the invention.

Pigments, Vat dyes, and Sulfur Dyes: Vat and sulfur dyes are hybrids between dyes and pigments, they are typically used to dye cotton and other cellulose-based fibers. In their chemically reduced ("leuco") forms they are water-soluble dyes, but when oxidized they become insoluble pigments. In conventional fiber dyeing, the fibers are exposed to the dyes in reduced form, which facilitates penetration of the dyes into the fiber. The fibers are then exposed to oxidizing conditions, which induce the formation of insoluble particles adsorbed within the fibers. This hybrid behavior provides a variety of methods in which these dyes may be used as colorants in the sheathing formulation.

In a one-step method, a pigment or oxidized vat or sulfur dye is dispersed into a protein sheathing formulation. Optionally, a surfactant may be included to aid in the dispersion. A viscous base sheathing formulation is also helpful in aiding dispersion lifetime by slowing the rate of settling. The colorant may be added as a solid powder or as an aqueous dispersion. In both cases but particularly the latter it is desirable that the addition of colorant not dilute the sheathing formulation to the extent that the sheath loses durability or does not effectively provide its properties when applied to the substrate. Aqueous dispersions of pigments are available from BASF under the trade-name of HiFast™. The colored sheathing formulation is then applied to the substrate and cured in place. The colorant is dispersed throughout the sheathing layer and is held in place by physical encapsulation.

In another one-step method, a leuco vat or sulfur dye solution is added to the sheathing formulation and the combined formulation is then oxidized to form a dispersion of colorant within the sheathing formulation. Optionally, the pH of the colored sheathing

formulation may need to be adjusted within the specifications required for the base sheathing formulation. This method provides for partial encapsulation of the sheathing polymer material within the oxidized particles. As above, a viscous base sheathing formulation is helpful in aiding dispersion lifetime by slowing the rate of particle settling. The resultant dispersion is then applied to a substrate, which is then cured to affix the sheathing layer. The encapsulated colorants are held fast by physical entanglements.

In another one-step method, one or more of the sheathing material components are added to a solution of a leuco, vat or sulfur dye. Preferably the component(s) are added in an amount equivalent to their weight percentage in the base sheathing formulation. More preferably, the addition of the components significantly increases the viscosity of the solution. The leuco dye is then oxidized to form a dispersion of particles, preferably partially encapsulating the sheathing material component(s). If required, the remaining components of the base sheathing formulation are added and the pH is adjusted to the required specification for cross-linking. The colored formulation is then applied to a substrate, and the substrate is cured to affix the sheathing layer. The encapsulated colorants are held fast by physical entanglements.

Other embodiments of this dyeing method are easily recognizable; although not described, all such are considered to be within the scope of the invention.

Modified Reactive Dyeing: Commercially available reactive dyes are typically used to dye cotton and wool fibers. They contain functional groups that react with nucleophilic sites under conditions of highly alkaline pH and elevated temperature. They are extremely colorfast, as the dye becomes covalently bound to the fiber. In the present invention, the sheathing material may not include appropriate reactive sites or may not be applied at highly alkaline pH, either case prevents reaction with commercial reactive dyes. Another challenge in the use of reactive dyes is hydrolysis of the reactive sites; hydrolysis competes with the cellulosic hydroxyl groups for reactivity of the dye and leads to inefficient dye use.

A variety of approaches may be employed to circumvent the difficulties described above. In one approach, the dye is first modified by reaction with a bifunctional reagent; one functional group of the reagent reacts with the dye, the other binds to the sheathing material. The modified dye is then added to a base protein sheathing formulation that can then be applied to a substrate in a one-step method. In another approach, a bifunctional reagent is added to a base sheathing formulation. the bifunctional reagent has one functional group that reacts preferentially with a reactive dye, the other binds to the sheathing material. The modified sheathing formulation is applied to the substrate and cured to affix the sheathing layer and bind the reagent. The treated substrate is then dyed with a reactive dye in a multiple-step method, wherein the reactive dye reacts preferentially with the remaining

functional group of the reagent. In yet another approach, the sheathing formulation incorporates one bifunctional reagent and the reactive dye is modified with a second bifunctional reagent. The two reagents each contain at least one functional group which reacts preferentially with a functional group of the other reagent. Either a one-step or multiple-step application may be envisioned in this case. Similar ideas have been presented by Lewis and Vigo (Lewis, D.M., Lei, X.; AATCC International Conference and Exhibition Book of Papers, Oct 4-7, 1992, pp. 259-265; Vigo, T.L., Blanchard, E.J.; AATCC International Conference and Exhibition Book of Papers, 1996, pp. 203-208; Vigo, T.L., Blanchard, E.J.; Textile Chemist and Colorist, vol. 19, No. 6 (1987); U.S. Pat. 4,678,473); however in these cases a cellulosic fiber is modified rather than a protein sheathing layer.

Examples of functional groups that react preferentially with reactive dyes include amines and thiols; these groups are much better nucleophiles than water and can eliminate wasteful hydrolysis. Amines are more preferred. Examples of functional groups that can react with components of a protein sheathing layer include, but are not limited to, hydroxyls, amines, thiols, epoxides, and blocked isocyanates. Non-limiting examples of bifunctional reagents include ethylene diamine, ethanolamine, and glycidol.

Other embodiments of this dyeing method are easily recognizable; although not described, all such are considered to be within the scope of the invention.

EXAMPLES

Experimental Measurements:

Wet Times: All wet times are the average of six measurements. All times given are the time needed for a drop of distilled water placed on the sample to be fully absorbed. All times greater than 120 sec were recorded and averaged as 120 sec. During measuring, all samples were elevated so that neither the upper nor the lower surface of the sample was touching a solid surface.

Example 1: Preparation of a Wool Protein Solution

Wool fabrics (7kg) were placed in an aqueous bath of 30% (by weight) hydrogen peroxide (100L), the pH of the bath being adjusted to 8 using aqueous ammonia. After 10 minutes, a severe heat generation and foaming arose naturally, and almost all of the wool fibers were dissolved completely after 40 minutes. Trace amounts of an insoluble residue were removed by filtration. To the resulting solution, 3 wt% epichlorohydrin was added as the crosslinker, and the pH was adjusted to 9 with sodium borate.

Example 2: Treatment of a Synthetic Fabric

Sanded microdenier polyester fabric (Burlington Industries, Greensboro, NC) was chosen as the synthetic substrate. The polyester was dipped in the protein solution from Example 1 and padded to 40-50% wet pickup and dried. The fabric was then sprayed with a 1 wt% solution of sodium hydrosulfide reducing agent to 40% wet pickup. The fabric was dried and cured at 350°F for 2 minutes. The fabric was then rinsed with warm water to remove unreacted chemical and again dried. The resulting treated fabric had the same hand as wool and was not shiny like the original polyester. Wet time by water was significantly improved (from >120 sec prior to treatment, to <10 sec after treatment). The fabric was laundered 20 times and still maintained the wool hand and wrinkle-free properties of the polyester. It also did not shrink, felt, pill, or lose its hydrophilic nature.

Example 3: Preparation of protein solution.

Protein solutions were prepared by dissolving granular gelatin (Acros Organics, a division of Fischer Scientific) in water with a dimethyloldihdroxyethyleneurea (DMDHEU) cross-linker (Patcorez™ P-53, BF Goodrich) and a wetting agent (WetAid NRW™ from BF Goodrich), at concentrations detailed in the following Examples. The solutions was kept warm (>30°C) during use.

Example 4: Application of protein solution to woven 100% polyester fabric.

A solution was prepared as described in Example 3 containing 10% by weight gelatin, 5% by weight DMDHEU, and 0.1% wetting agent. A swatch of 100% polyester woven fabric was dipped into the warm solution, padded to a level of 60% wet pick-up, and dried at 195°F. The fabric was then cured at 335°F for 30 seconds.

The resulting fabric was initially stiff due to excess chemical on the surface, but after one home laundering the fabric became soft and drapable. The hand did not change significantly between 2 and 25 home launderings. At 25 home launderings the hand remained fuller and firmer than the untreated polyester alone. Wet times were measured for the sample:

Results: Wet Times after multiple home launderings.

Wet Tim s	Treated	Untreated
0HL	8.2 sec	>120 sec
1HL	3.2 sec	>120 sec
5HL	8.3 sec	>120 sec
10HL	13.3 sec	>120 sec
25HL	18.3 sec	>120 sec

Example 5: Application of protein solution to woven 100% wool fabric.

A solution was prepared as described in Example 3 containing 10% by weight gelatin, 5% by weight DMDHEU, and 0.1% wetting agent. A swatch of 100% wool woven fabric was dipped into the warm solution, padded to a level of 60% wet pick-up, and dried at 195°F. The fabric was then cured at 335°F for 30 seconds.

The shrinkage of the wool sample was measured in the warp and fill directions and reported as a percent change compared to the sample prior to laundering. The samples were measure after repeated home launderings and tumble dryings. The treated samples shrank less than the untreated wool.

Results:

Shrinkage (warp/fill)	Treated	Untreated
1HL	3.2% / 1.6%	7.6% / 8.9%
5HL	3.3% / 1.2%	8.8% / 9.8%
10HL	4.0% / 2.3%	12.5% / 14.3%

WHAT IS CLAIMED IS:

1. A composite fibrous substrate comprising core fibers and a protein sheath attached around the individual cor fibers and wherein the protein sheath is adhered to itself by covalent bonds.

2. A composite fibrous substrate according to claim 1 wherein the protein sheath further comprises at least one auxiliary component.

3. A composite fibrous substrate comprising core fibers and a protein sheath attached around the individual core fibers, and wherein the fibrous substrate is prepared by the process of:

contacting a fibrous substrate comprising core fibers with an aqueous solution of water-soluble protein and a crosslinker and, optionally, a suitable crosslinker catalyst;

optionally, contacting the fibrous substrate with an acidic reducing agent that regenerates the original insoluble protein structure;

heating the fibrous substrate to dryness; and

curing at a temperature sufficient to cause reaction between the crosslinker and the protein.

4. A composite fibrous substrate according to claim 3 wherein the aqueous solution further comprises at least one auxiliary component.

5. A composite fibrous substrate according to claim 3 wherein the process further comprises the step of reacting the protein sheath with at least one auxiliary component to bind the auxiliary component onto or within the protein sheath.

6. A composite fibrous substrate according to claim 2, 4 or 5 wherein the auxiliary component is selected from the group consisting of colorants, metal colloids, magnetic colloids, infrared-absorbing compounds, ultraviolet light-blocking compounds, bioactive agents, flame-retardant chemicals, anti-static agents, odor-absorbing compounds, neutralizers, and hydrolyzable linkers.

7. A composite fibrous substrate according to any one of claims 1 to 6 wherein the core fibers are synthetic fibers.

8. A composite fibrous substrate according to any one of claims 1 to 6 wherein the core fibers are man-made fibers.

9. A composite fibrous substrate according to any one of claims 1 to 6 wherein the core fibers are natural fibers.

10. A method of preparing a composite fibrous substrate, the method comprising the steps of:

contacting a fibrous substrate comprising core fibers with an aqueous solution of water-soluble protein and a crosslinker and, optionally, a suitable crosslinker catalyst;

optionally, contacting the fibrous substrate with an acidic reducing agent that regenerates the original insoluble protein structure;

heating the fibrous substrate to dryness; and

curing at a temperature sufficient to cause reaction between the crosslinker and the protein;

to give a composite fibrous substrate comprising a protein sheath attached around the individual fibers of the substrate and wherein the protein sheath is adhered to itself by covalent bonds.

11. A method according to claim 10 wherein the aqueous solution further comprises at least one auxiliary component.

12. A method according to claim 10 which further comprises the step of reacting the protein sheath with at least one auxiliary component to bind the auxiliary component onto or within the protein sheath.

13. A method according to claim 11 or 12 wherein the auxiliary component is selected from the group consisting of colorants, metal colloids, magnetic colloids, infrared-absorbing compounds, ultraviolet light-blocking compounds, bioactive agents, flame-retardant chemicals, anti-static agents, odor-absorbing compounds, neutralizers, and hydrolyzable linkers.

14. A method according to any one of claims 10 to 13 which further comprises the step of treating the composite fibrous substrate with a post-processing treatment generally used on wool.

15. A method according to any one of claims 10 to 14 wherein the core fibers are synthetic fibers.

16. A method according to any one of claims 10 to 14 wherein the core fibers are man-made fibers.

17. A method according to any one of claims 10 to 14 wherein the core fibers are natural fibers.